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# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improvements in or relating to the treatment of Metal Surfaces

We, THE PYRENE COMPANY, a British Company, of Great West Road, Brentford, Middlesex, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that maleic anhydride forms water-soluble copolymers with various aliphatic vinyl compounds, including methyl vinyl ether, and that these copolymers can be made to react with polyhydroxy compounds to yield water-insoluble cross-linked products.

We have found that it is possible to form clear, stable aqueous solutions containing a copolymer of maleic anhydride with methyl vinyl ether, hydroxyethyl cellulose and phosphoric acid, and that such solutions can be applied to metal surfaces to yield adherent water-insoluble coatings. It is an important advantage of these solutions that they do not gel upon standing for a few days, as we have found to be the case when hydroxyethyl cellulose is replaced by starch. The solutions are particularly well suited to applying protective coatings to ferrous surfaces and zinc-containing surfaces. On the latter surfaces the coatings confer a high degree of protection against white rusting without detracting from the bright metallic appearance of the surface.

For protecting metallic surfaces, in particular those of ferrous metals, with which the phosphoric acid reacts to form a protective coating of iron phosphate, it is important that the aqueous solution should wet the metal surface efficiently. To obtain good wetting we find that it is important to control the viscosity of the solutions. Surprisingly, we find that whereas a solution of the methyl vinyl ether/maleic anhydride copolymer and hydroxyethyl cellulose wets a metal surface over only a limited range of viscosities, when phosphoric acid is also present in the solution the range of viscosity over which the composition wets metal surfaces is substan-

tially increased. In general, the viscosity of the solution should be from 50 to 100 centipoises and preferably from 57 to 80 centipoises. We prefer to use a grade of the copolymer known under the trade mark "Gantrez AN 139."

Preferred solutions according to the invention contain sufficient of the copolymer and hydroxyethyl cellulose to yield solutions having a viscosity within one of the above ranges, and from 1 to 3% by weight of phosphoric acid.

The wetting properties of the aqueous solution may be improved by the incorporation of a wetting agent. We find, however, that cationic and anionic wetting agents are less suitable since they tend to lead to rusting at the edges of a ferrous surface being treated. However, non-ionic wetting agents may with advantage be incorporated in the solution, say in an amount of from 0.1% to 0.5% by weight.

The solution may be applied to a metal surface by any conventional method, such as spraying, brushing, dipping or flooding. After allowing any excess of the solution to drain from the metal surface, the coating may be allowed to dry and is preferably subsequently stoved to effect the cross-linking reaction and render the coating insoluble in water. This curing can be allowed to occur at room temperature, but it tends to be rather slow.

Improved corrosion resistance can be imparted to a metal surface by including in a solution according to the invention a small proportion, say from 1 to 5% by weight as  $\text{CrO}_3$ , of a water-soluble hexavalent chromium compound, such as chromic acid or ammonium dichromate. A suitable quantity of chromic acid in the solution is about 1% to 5% by weight as  $\text{CrO}_3$ . An advantage of using ammonium dichromate is that a smaller quantity of the compound produces the equivalent effect, 1 to 3% generally being sufficient. Unlike, say, sodium dichromate, it decomposes dur-

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ing stoving to leave no water-soluble residue.

When a solution containing no hexavalent chromium is applied to a ferrous surface rusting is liable to commence unless the surface is stoved within 30 seconds of the application of the solution. When a hexavalent chromium is present, however, the period between application of the solution and stoving can be extended very considerably, for example for periods as long as one or two weeks.

Metal surfaces coated with one of the above solutions generally require stoving for substantial periods at elevated temperatures to effect curing. This can be a considerable disadvantage, and it is desirable that the cross-linking reaction should proceed readily. We have surprisingly found that if a soluble condensed phosphate is also present in the solution the cross-linking reaction is substantially accelerated. The alkali metal pyrophosphates have a good accelerating action, but we find that zinc pyrophosphate is even better, so that considerably less of this compound can be used to achieve a given degree of acceleration. In general we find that a suitable quantity of alkali metal pyrophosphate is from 0.1 to 1.5% by weight, while equivalent results are obtained with from 0.055 to 0.5% by weight of zinc pyrophosphate. No substantial improvement is obtained when greater quantities than these are used. Both sodium hexametaphosphate and sodium tripolyphosphate have an accelerating effect, but considerably higher concentrations are necessary, and these condensed phosphates are therefore not so conveniently used. When the metal surface is a zinc surface the cross-linking reaction takes place sufficiently rapidly for it to be unnecessary to use a condensed phosphate accelerator.

The quantities of methyl vinyl ether/maleic anhydride copolymer and hydroxyethylcellulose which may be present in a solution according to the invention depend upon

the average molecular weight of each. It is simply important there should be sufficient of these constituents to form a coating and that the resultant solution should adequately wet the surface being coated. For example, we find that a suitable quantity of the copolymer sold under the trade mark Gantrez AN 139 is from 0.75 to 2% by weight. By making suitable allowance for changes in viscosity the grades identified by the letters AN 119 and AN 169 can be substituted for AN 139. We also find that whereas from 0.25 to 1% by weight of that grade of hydroxyethyl cellulose marketed by Union Carbide Corporation under the designation QP 4400 is sufficient, if the grade known as WP09 is used the solution tolerates more of it (e.g. 3% WP09 for 0.5% QP 4400). As stated above, in any given case it is preferred that the viscosity of the solution should be from 57 to 80 centipoises.

The following examples illustrate the invention:—

#### EXAMPLE 1

A particularly valuable coating solution is that having the following basic composition:

1% by weight of methyl vinyl ether/maleic anhydride copolymer (GANTREZ AN 139)

0.5% by weight of hydroxyethyl cellulose (QP 4400)

1.0% by weight of ammonium dichromate

2.0% by weight of phosphoric acid

0.2% by weight of an ethylene oxide condensate of nonyl phenol containing 10 ethylene oxide units

Viscosity—60 centipoises

To illustrate the effect of condensed phosphates on the stoving conditions necessary to produce adherent water-insoluble films on a steel surface, varying amounts of sodium pyrophosphate decahydrate were used as accelerator. The following results were obtained.

Quantity of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ added	Stoving Conditions
nil	480°F for 5 minutes
0.1%	250°F for 30 minutes
0.5%	180°F for 15 minutes
1.0%	120°F for 30 minutes
1.5%	120°F for 15 minutes

In addition, when 0.5% of sodium pyrophosphate was used, the films became water-insoluble at room temperature after 12 hours.

When 0.1% of zinc pyrophosphate was used instead of sodium pyrophosphate water-insoluble films were produced in 3 hours at room temperature.

The following five examples all illustrate solutions according to the invention. In each the non-ionic wetting agent was the same as that of Example 1. Furthermore in each sodium and zinc pyrophosphate can be interchanged, 0.1% of the zinc salt being equivalent to 0.5% of the sodium salt.

Example	2	3	4	5	6
Gantrez AN 139	0.75%	1%	2%	0.5%	0.5%
Hydroxyethylcellulose (QP 4400)	0.75%	0.25%	0.5%	1.25%	1%
Chromium dichromate	1%	1%	1%	1%	1%
Phosphoric acid	2%	2%	2%	2%	2%
Nonionic wetting agent	0.2%	0.2%	0.2%	0.2%	0.2%
Sodium pyrophosphate	0.5%	—	0.5%	—	—
Zinc pyrophosphate	—	0.1%	—	0.1%	0.1%
Viscosity in centipoises	66	50	70	100	80

## EXAMPLE 7

This example illustrates the use of the solution of Example 1 containing no pyrophosphate, to form a coating on a zinc surface.

- Hot dip galvanised steel panels were preheated to approximately 60°C in an oven and then were sprayed immediately with the solution by means of a ring of spray jets. As soon as the panels were cool, the coating had hardened sufficiently for handling. After exposure for 200 hours at 100% humidity and 50°C the panels had retained their bright shiny appearance whereas similar untreated panels, subjected to the same test, were completely covered by a film of white rust.

## WHAT WE CLAIM IS:—

1. A process in which a coating is applied to a metal surface from an aqueous solution containing a copolymer of maleic anhydride with methyl vinyl ether, hydroxy ethyl cellulose and phosphoric acid and the coating is converted to a water-insoluble state.
2. A process according to claim 1 in which the coating is rendered water-insoluble by stoving.
3. A process according to claim 1 or claim 2 in which the aqueous solution has a viscosity of from 50 to 100 centipoises.
4. A process according to claim 3 in which the solution has a viscosity of from 57 to 80 centipoises.
5. A process according to any one of the preceding claims in which the aqueous solution contains from 1 to 3% by weight of phosphoric acid.
6. A process according to any one of the preceding claims in which the aqueous solution contains from 0.1 to 0.5% by weight of a non-ionic wetting agent.
7. A process according to any one of the

preceding claims in which the aqueous solution contains a small proportion of a water-soluble hexavalent chromium compound.

8. A process according to claim 7 in which the aqueous solution contains from 1 to 5% by weight of chromic acid at CrO<sub>3</sub>, or from 1 to 3% by weight of ammonium dichromate.

9. A process according to any one of the preceding claims in which the aqueous solution contains a condensed phosphate.

10. A process according to claim 9 in which the condensed phosphate is an alkali metal pyrophosphate or zinc pyrophosphate.

11. A process according to claim 10 in which the quantity of alkali metal pyrophosphate in the solution is from 0.1 to 1.5% by weight.

12. A process according to claim 10 in which the quantity of zinc pyrophosphate in the solution is from 0.05 to 0.5% by weight.

13. A process according to any one of the preceding claims in which the metal surface treated is a ferrous metal surface.

14. A process according to any one of claims 1 to 8 in which the metal surface treated is a zinc-containing surface.

15. A process according to claim 1 substantially as herein described with reference to Example 1.

16. A process according to claim 1 substantially as herein described with reference to Example 7.

17. An aqueous solution containing from 1 to 3% by weight of phosphoric acid, hydroxy ethyl cellulose, and a copolymer of maleic anhydride with methyl vinyl ether, the quantities of the last two ingredients being such as to yield a solution having a viscosity of from 50 to 100 centipoises.

18. A solution according to claim 17 in which the viscosity of the solution is from 57 to 80 centipoises.

19. A solution according to claim 17 or claim 18 containing from 0.1 to 0.5% by weight of a non-ionic wetting agent.
20. A solution according to any one of claims 17 to 19 containing from 1 to 5% by weight of a water-soluble hexavalent chromium compound (expressed as  $\text{CrO}_3$ ).
21. A solution according to any one of claims 17 to 20 containing a condensed phosphate.
22. A solution according to claim 21 containing from 0.1 to 0.5% by weight of an alkali metal pyrophosphate.
23. A solution according to claim 21 containing from 0.05 to 0.5% by weight of zinc pyrophosphate.
24. A solution according to claim 17 substantially as herein described in any of Examples 1 to 6.
25. A metal article, the surface of which is coated by the process claimed in any one of claim 1 to 16.
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